

OCCURRENCE AND CRYSTAL STRUCTURE OF KIPUSHITE, A NEW COPPER-ZINC PHOSPHATE FROM KIPUSHI, ZAIRE

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ABSTRACT

Kipushite occurs in the oxidation zone of the deposit of Kipushi, southern Shaba, Zaire, in association with other secondary minerals of Cu, Zn and Pb. It appears as aggregates of subparallel prisms or, rarely, as isolated {111} prisms elongated along $[10\bar{1}]$, emerald green in color, transparent to translucent. Optics: biaxial (-), $2V = 23^\circ$ (calc.), $\alpha 1.693(2)$, $\beta 1.738(2)$ and $\gamma 1.740(2)$. It is monoclinic $P2_1/c$, with $a 12.197(2)$, $b 9.156(2)$, $c 10.667(2)$ Å, $\beta 96.77(2)^\circ$, $Z = 4$, density 3.904 (calc.) and 3.80 (meas.) g/cm^3 . The strongest six reflections in the X-ray powder pattern [d in Å(hkl)] are 4.03(100)(300,12 $\bar{1}$), 2.554(90)(132), 2.970(60)(32 $\bar{1}$,130), 1.531(60b)(72 $\bar{3}$,136,036,060), 12.2(50)(100) and 3.386(50)(12 $\bar{2}$,221,311). An electron-microprobe analysis gave CuO 43.0, ZnO 24.4, P₂O₅ 20.9, H₂O (by thermogravimetry) 11.1, total 99.4%, yielding the formula 6[(Cu,Zn)O]₅•P₂O₅•4H₂O. The Cu:Zn ratio is equal to 1.8:1.0 (mean value); it ranges from 1.1 to 2.6. The crystal structure was determined by X-ray diffraction ($R = 0.05$ for 1252 reflections). It consists of two sheets containing octahedra and tetrahedra in [(Cu,Zn)₅(OH)₅(H₂O)PO₄]²⁺ units and one sheet of tetrahedra [Zn(OH)PO₄]²⁻. The sheets are connected by shared apical oxygen atoms of PO₄ and ZnO₃(OH) tetrahedra and by hydrogen bonds. The structural formula is (Cu,Zn)₅Zn(OH)₆(H₂O)(PO₄)₂.

Keywords: kipushite, copper, zinc, phosphate, mineralogical description, crystal structure, Zaire.

SOMMAIRE

La kipushite se trouve associée à des minéraux secondaires de cuivre, de zinc et de plomb dans la zone d'oxydation du gisement de Kipushi, Shaba méridional, Zaïre. Elle se présente en agrégats de prismes subparallèles ou, rarement, en prismes isolés {111} allongés suivant $[10\bar{1}]$, de couleur vert émeraude, transparents à translucides. Optique: biaxe (-), $2V = 23^\circ$ (calculé), $\alpha 1.693(2)$, $\beta 1.738(2)$ et $\gamma 1.740(2)$. Système monoclinique, groupe spatial $P2_1/c$, avec $a 12.197(2)$, $b 9.156(2)$, $c 10.667(2)$ Å, $\beta 96.77(2)^\circ$ et $Z = 4$. Densité: 3.904 (calculée) et 3.80 (mesurée). Les

six raies les plus intenses du diagramme de poudre [d en Å(hkl)] sont: 4.03(100)(300,12 $\bar{1}$), 2.554(90)(132), 2.970(60)(32 $\bar{1}$,130), 1.531(60b)(72 $\bar{3}$,136,036,060), 12.2(50)(100) et 3.386(50)(12 $\bar{2}$,221,311). La composition chimique déterminée à la microsonde électronique: CuO 43.0, ZnO 24.4, P₂O₅ 20.9, H₂O (par thermogravimétrie) 11.1, total 99.4%, donne la formule 6[(Cu,Zn)O]₅•P₂O₅•4H₂O. Le rapport Cu:Zn moyen est de 1.8/1.0, mais varie de 1.1 à 2.6. La structure a été déterminée par diffraction X ($R = 0.05$ pour 1252 réflexions). Elle comporte deux feuillets mixtes d'octaèdres et de tétraèdres [(Cu,Zn)₅(OH)₅(H₂O)PO₄]²⁺ et un feuillet de tétraèdres [Zn(OH)PO₄]²⁻. Les feuillets sont unis par les sommets communs aux tétraèdres PO₄ et ZnO₃(OH) et par des liaisons hydrogène. La formule structurale s'écrit (Cu,Zn)₅Zn(OH)₆(H₂O)(PO₄)₂.

Mots-clés: kipushite, cuivre, zinc, phosphate, description minéralogique, structure cristalline, Zaïre.

INTRODUCTION

The Kipushi deposit is located about 30 km southwest of Lubumbashi, southern Shaba, Zaire, near the border with Zambia. The metallic ores have been worked for more than sixty years. The mineralization consists of Zn, Pb, Cu and Fe sulfides with accessory Ga, Ge, Mo, W and V. It occurs in the dolomite and schist-dolomite series of the Lower Kundelunguan (Precambrian IV). The mineralization is mainly located along a transverse fault that cuts the flank of an asymmetric anticline. A complete description of the geology and the mineralogy of the Kipushi deposit has been given by Intiomale & Oosterbosh (1974).

The thickness of the weathered zone extended to about 100 metres in depth; this zone has now been completely mined out. The most abundant minerals of that zone were cerussite, malachite, smithsonite, hemimorphite, cuprite and hematite, with a rich association of accessory Cu-Zn-Pb-Fe phosphates, car-

TABLE 1. SUMMARY DATA FOR VESZELYITE AND THE IDENTICAL MINERAL SPECIES

	Theoretical	Veszelyite		Arakawaite	Veszelyite from Kipushi
	1	2	3	4	5
CuO	38.20	37.82	37.34	40.44	35.99
ZnO	26.05	26.69	25.20	23.64	28.94
[CuO + ZnO]	64.25	64.51	62.54	64.08	64.93
P ₂ O ₅	18.93	18.43	9.01	19.01	19.90
As ₂ O ₅	—	—	10.41	—	—
H ₂ O	16.82	16.87	17.05	16.22	14.31
var.	—	0.11	—	—	0.65
	100.00	99.92	99.01	99.31	99.79
Cu : Zn	3 : 2	3 : 2	3 : 2	5 : 3	5 : 4
Density g/cm ³	3.38	3.34	3.53	3.09	3.37
Refractive indices		α 1.640	1.618		
		β 1.658	1.622		1.63-1.64
		γ 1.695	1.658		
ZV		71° (+)	38.5° (+)		

Data for Arakawa specimen (6) : monoclinic $P2_1/a$, $Z = 4$ [(Cu_{1.6}Zn_{1.2})PO₄(OH)₂·2H₂O], a_0 9.828(3), b_0 10.224(3), a_0 7.532(3)Å, β 103.18(2)° Density (calc.) 3.38 g/cm³.

1 : theoretical composition for (Cu,Zn)₃(PO₄)₂(OH)₂·2H₂O, Cu:Zn = 3:2.
2 : Zsivny (1930, 1932). 3 : Schrauf (1880) with optical data of Larsen (1921). 4 : Wakabayashi & Komada (1921). 5 : Buttgenbach (1927). 6 : Ghose *et al.* (1974).

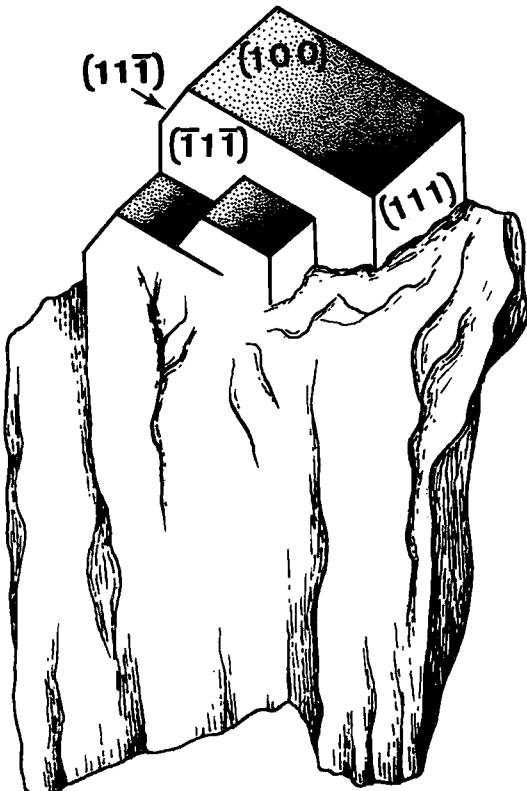


FIG. 1. Aggregates of kipushite prisms.

bonates, silicates, sulfates and vanadates. The holotype specimen of kipushite is registered in the mineralogical collection of the Musée royal de l'Afrique centrale (No. 14.026). A cotype exists in a private collection. The mineralogical association of kipushite includes pseudomalachite in dark blue nodules, earthy pale green malachite, blue and green hemimorphite, colorless sticks of pyromorphite, ultramarine crystalline masses of veszelyite, yellow and olive green crusts of vauquelinite, acicular crystals clusters of libethenite, quartz and iron oxides.

VESZELYITE AND IDENTICAL MINERAL SPECIES

Data on the hydrated phosphates of copper and zinc belonging to the (Cu,Zn)₃PO₄(OH)₂·nH₂O group are summarized by Palache *et al.* (1951). All these minerals are generally well crystallized and transparent to translucent. Their color varies from ultramarine blue to bluish green. The first description published pertained to veszelyite from Moravicza in Roumania (Schrauf 1880); the composition published shows a considerable amount of As (10.41% As₂O₅). Half a century later, two additional descriptions were published: an unnamed mineral from Broken Hill in Zambia (Mennell & Spencer 1920), and arakawaite from the Arakawa mine, Japan (Wakabayashi & Komada 1921). Ohashi (1924) showed that arakawaite is similar to the unnamed mineral from Broken Hill. Buttgenbach (1927) studied several crystals from Prince Leopold mine, Kipushi, southern Shaba, Zaire; he gave these crystals the preliminary name "kipushite" in order to facilitate their description and their comparison with similar species. Nevertheless, he regarded "kipushite" as identical to the unnamed mineral from Broken Hill and very close to arakawaite and veszelyite, with which it would constitute an isomorphous series. Zsivny (1930, 1932) reinvestigated the type material from Moravicza; his new chemical analysis showed that there is no arsenic in veszelyite and, for that reason, the similarity between veszelyite, the unnamed mineral from Broken Hill, arakawaite and the Cu-Zn phosphate from Kipushi was established. The only difference concerns the Cu:Zn ratio. Zsivny (1932) retained the name veszelyite because of chronological priority. Berry (1948) calculated the unit-cell constants and gave the space group of veszelyite from Moravicza. Ghose *et al.* (1974) studied the crystal structure of a specimen from Arakawa and showed the existence of a new type of sheet structure. Chemical and optical data, as well as the densities given by the various authors, are summarized in Table 1. Crystallographic data of Ghose *et al.* (1974) are also shown in Table 1.

THE USE OF THE NAME KIPUSHITE

As the identity of the mineral from Kipushi studied by Buttgenbach (1927) with veszelyite is established, the provisional name *kipushite* used by that author is free for another mineral. We apply this name to the new Cu-Zn phosphate described in this paper. The name of the Kipushi mine, famous for its rich mineralogical associations, will then appear in the literature applied to a well-defined and unique mineral species.

The description (17/1) and the name (14/4) of the mineral have been approved by the Commission on New Minerals and Mineral Names, IMA (September 1983).

MORPHOLOGY AND PHYSICAL PROPERTIES

Kipushite is emerald green in color, with a pale blue streak; it is transparent to translucent and has a vitreous luster. It appears as more or less elongate aggregates of prisms up to 3 mm (Fig. 1) or, rarely, as isolated prismatic crystals up to 0.3 mm (Fig. 2), of which lateral faces are uneven and rounded. Prisms $\{111\}$ are elongate along $[10\bar{1}]$ and terminated principally by (100) . The other often-present forms are $\{102\}$, $\{01\bar{2}\}$ and $\{11\bar{1}\}$. The measurable angles between vectors are: $(111)\wedge(\bar{1}\bar{1}\bar{1})$ 101.0° , $(111)\wedge(100)$ 56.9° . There are no distinct cleavages, and the fracture is uneven. The Mohs hardness is approximately 4. Density is 3.8 (measured in Clerici solution) and 3.904 g/cm^3 (calculated).

The mineral is biaxial negative with a small $2V$ (not measured; 23° calculated) and the indices of refraction (sodium D line) are: α 1.693(2) (colorless), β 1.738(2) (blue) and γ 1.740(2) (bright blue). Sign of elongation and optical orientation were not determined owing to the lack of cleavage.

CHEMICAL COMPOSITION

Quantitative chemical analysis by electron microprobe (Centre d'analyse par microsonde pour

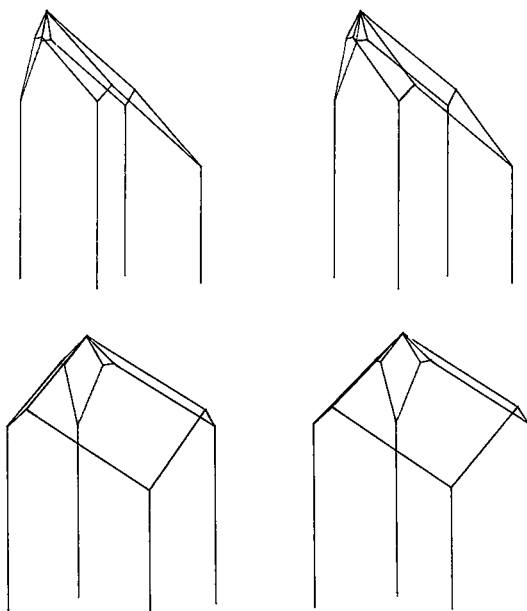


FIG. 2. Two stereoscopic views of a kipushite crystal. Lateral faces (idealized): $\{111\}$, lozenge: (100) , kite: $(\bar{1}0\bar{2})$, trapezes: (111) and $(\bar{1}\bar{1}\bar{1})$, triangles: $(01\bar{2})$ and $(0\bar{1}\bar{2})$.

les Sciences de la terre, Laboratoire de pétrographie, Université Catholique de Louvain; J. Wautier, analyst) has been carried out with the following standards: Cu_2O for copper, willemitte for zinc, and apatite for phosphorus. Water was measured by thermogravimetry (Stone apparatus with Cahn balance). The results are given in Table 2. The TGA curve in Figure 3 shows the loss of structural water between 320 and 450°C . The formula is $(\text{Cu}, \text{Zn})_6(\text{PO}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$, with $\text{Cu}:\text{Zn} = 1.80:1$. The $\text{Cu}:\text{Zn}$ ratio is not fixed in this mineral species; it varies between $2.6:1$ and $1.1:1$ in the grains analyzed.

TABLE 2. THE CHEMICAL COMPOSITION OF KIPUSHITE, AS DETERMINED BY ELECTRON MICROPROBE

	1	2	3	4	5
CuO	36.4 48.3 48.0 36.3 35.2 36.6 35.5	45.8 48.0 47.3 48.4 42.9 45.4 48.4	43.0	3.77	44.1
ZnO	31.0 19.4 21.9 34.0 30.2 29.6 31.6	21.3 18.5 19.5 20.5 25.1 20.9 18.5	24.4	2.09	25.1
P_2O_5	20.8 20.8 20.8 22.1 21.3 20.5 21.0	20.8 21.1 20.7 21.3 20.4 20.6 20.7	20.9	1.03	20.4
H_2O			11.1	4.30	10.4
			99.4		100.0

1 and 2 : experimental weight percentages of two crystals. 3 : mean values (H_2O by thermogravimetry). 4 : molecular ratio for 11 atoms of oxygen in the anhydrous part. 5 : expected composition (wt. % oxides) for $(\text{Cu}, \text{Zn})_6(\text{PO}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$, with $\text{Cu}:\text{Zn} = 1.8:1$.

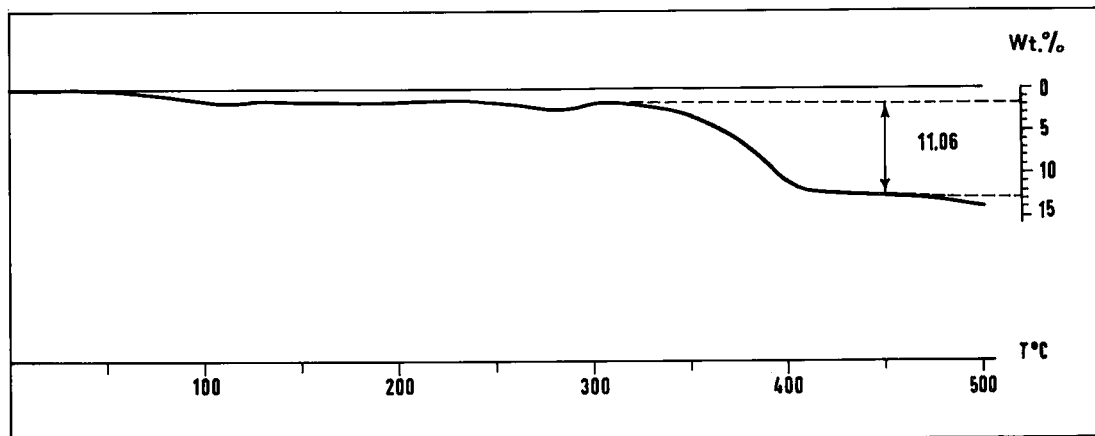


FIG. 3. Results of thermogravimetric analysis of kipsushite.

COMPATIBILITY INDEX

The compatibility index (Mandarino 1981) was calculated from the following data: formula 3.86 CuO , 2.14 ZnO , P_2O_5 , $4\text{H}_2\text{O}$; $M = 695.2$; $V = 1183 \text{ \AA}^3$; $D_{\text{calc}} = 3.904 \text{ g/cm}^3$; $\bar{n} = 1.724$; $K_p = 0.1855$ and

$K_C = 0.1873$. The value of $1 - (K_p/K_C)$ is 0.010, which is considered in the "superior" category.

X-RAY-DIFFRACTION DATA

Powder data, which are given in Table 3, are not similar to other listed data. The hkl indices were assigned in accordance with the measured single-crystal-diffractometer intensities. Cell parameters and space group were determined from Weissenberg and precession photographs. Parameters were refined by least squares using fifteen reflections measured on a 4-circle diffractometer. Kipsushite is monoclinic, space group $P2_1/c$, a 12.197(2), b 9.156(2), c 10.667(2) Å, β 96.77(2)°; $Z = 4$.

CRYSTAL-STRUCTURE DETERMINATION

The intensity of all reflections with $2\theta < 50^\circ$ was measured using a Syntex $P2_1$ four-circle diffractometer, $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), ω -scan from -1.1° to $+1.1^\circ$. Of the 2084 independent reflections collected, 1252 are classified as observed [$I > 2.5\sigma(I)$]. Because of the small dimensions ($< 0.1 \text{ mm}$) of the irregularly shaped crystalline fragment chosen for data collection and the low value of μ (10.9 mm^{-1}), no absorption correction was applied.

The structure was solved by the Patterson method. As the superposition method gave poor results owing to the numerous coincidences between interatomic vectors, the following process was used. All peaks that could correspond to $2x$, $2y$, $2z$ (for Cu and Zn) were located, starting from Harker peaks 0 , $\frac{1}{2} + 2y$, $\frac{1}{2}$ and $2x$, $\frac{1}{2}$, $\frac{1}{2} + 2z$. The co-ordinates x_p , y_p , z_i of all possible Cu and Zn positions were thus obtained. They were grouped in pairs. For each group, co-ordinates and temperature factors were refined by least squares. Then a difference-Fourier series was

TABLE 3. X-RAY POWDER PATTERN OF KIPUSHITE

hkl	d_{calc}	d_{obs}	I_{vis}	hkl	d_{calc}	d_{obs}	I_{vis}
100	12.1	12.2	50	31 $\bar{4}$	2.271	2.268	15
011	6.93	6.92	10	323	2.204	2.199	3
11 $\bar{1}$	6.22	6.18	20	42 $\bar{3}$	2.157	2.156	40
200	6.06	6.06	40	332	2.155		
210	5.05	5.05	25	40 $\bar{4}$	2.121	2.117	25
11 $\bar{2}$	4.44	4.45	3	24 $\bar{1}$	2.116		
211	4.39			521	2.057	2.060	30
120	4.28	142	2.054				
20 $\bar{2}$	4.24	24 $\bar{2}$	2.014				
300	4.04	4.03	100	13 $\bar{4}$	2.002	2.007	15
12 $\bar{1}$	4.03			034	2.000		
202	3.77	3.76	5	432	1.936	1.936	40
310	3.69	3.69	3	404	1.886	1.886	8
22 $\bar{1}$	3.531	3.526	20	125	1.868	1.862	15
12 $\bar{2}$	3.400	3.386	45	53 $\bar{2}$	1.841	1.837	10
221	3.379			25 $\bar{1}$	1.739	1.737	15
311	3.377	334	1.732				
11 $\bar{3}$	3.271	3.274	30	30 $\bar{6}$	1.692	1.688	15b
31 $\bar{2}$	3.196	3.198	8	504	1.691		
32 $\bar{1}$	2.982	2.970	60	630	1.684		
130	2.959			22 $\bar{6}$	1.635		
312	2.887	2.868	30b	053	1.626	1.628	10
41 $\bar{1}$	2.856			15 $\bar{3}$	1.623		
10 $\bar{4}$	2.653	2.654	40	72 $\bar{2}$	1.598	1.598	10
132	2.552	2.554	90	72 $\bar{3}$	1.537	1.531	60b
23 $\bar{2}$	2.477	2.477	5	13 $\bar{6}$	1.536		
330	2.435	2.430	15	036	1.528		
313	2.425			060	1.526		
42 $\bar{2}$	2.372	2.365	8	73 $\bar{2}$	1.489	1.483	10
30 $\bar{4}$	2.345	2.340	20	33 $\bar{6}$	1.480		

114.6 mm Debye-Scherrer camera, $\text{CuK}\alpha$ radiation, Ni filter, indexing based on single-crystal intensities. $d(hkl)$ in Å, visually estimated intensities.

calculated, and the one or two largest peaks were assumed to be atoms and introduced in the least-squares refinement. The examination of *R* values and, above all, of temperature factors (which may not become too small, too large or too different from each other) led to the choice at this stage of a good partial solution. The other atoms (Cu, Zn, P, O) were then easily found with the aid of successive Fourier series and least-squares refinement.

The final difference-Fourier synthesis shows only a few small peaks; these do not correspond to H atoms, or to displacement of atomic positions due to partial substitution of Cu by Zn. The final *R* factor is 0.047 for 1252 observed reflections and 0.092 for all 2084 reflections. A table of calculated and observed structure-factors has been deposited; a copy may be obtained on request to: Depository of Unpublished Data, CISTI, National Research Council

TABLE 4. ATOMIC COORDINATES ($\times 10^4$), B EQUIVALENT (\AA^2), U_{1j} ($\times 10^4$) (\AA^2)

X/A	Y/B	Z/C	BEQ	U11	U22	U33	U23	U13	U12	
Cu1	3307(2)	4140(2)	1945(2)	0.93	184(10)	59(10)	112(9)	27(8)	21(7)	38(10)
Cu2	2745(2)	2660(2)	4613(2)	1.04	200(9)	38(10)	143(10)	2(9)	-42(7)	-8(9)
Cu3	3280(2)	5854(2)	4483(2)	0.78	153(9)	30(10)	106(10)	3(8)	-19(8)	-12(9)
Cu4	3259(2)	7639(2)	1937(2)	0.79	154(9)	58(9)	91(9)	-9(8)	26(7)	-15(9)
Cu5	3118(2)	9349(2)	4345(2)	0.71	130(9)	30(10)	106(10)	-9(8)	-1(8)	-3(8)
Zn6	316(1)	943(2)	3355(2)	0.98	120(9)	115(10)	133(9)	10(8)	5(7)	-8(8)
P7	434(3)	2771(5)	1029(4)	0.89	89(18)	104(21)	140(21)	-4(17)	-4(15)	-7(16)
P8	4287(3)	872(4)	2010(3)	0.71	118(19)	56(19)	92(19)	22(16)	-5(15)	15(17)
O9	2485(8)	4320(10)	3416(9)	0.76	98(52)	1(51)	177(57)	12(44)	-40(44)	-65(43)
O10	4462(8)	5771(11)	2957(10)	0.96	133(53)	59(54)	167(56)	-15(45)	0(43)	-27(47)
O11	2541(8)	5889(11)	1052(9)	0.84	143(52)	113(55)	59(50)	-34(46)	-7(41)	-51(49)
O12	3821(8)	3929(11)	266(9)	0.91	162(54)	82(53)	95(53)	37(46)	-2(44)	-18(47)
O13	1568(9)	2090(13)	950(10)	1.66	226(62)	243(67)	178(60)	18(52)	97(49)	16(52)
O14	3937(8)	2287(12)	2630(9)	1.10	201(55)	198(63)	11(48)	12(47)	-21(43)	45(52)
O15	3755(7)	4146(11)	5608(9)	0.58	50(46)	21(50)	138(52)	-30(44)	-34(40)	48(44)
O16	1927(8)	1114(13)	3572(10)	1.36	84(50)	287(67)	124(53)	-18(53)	-73(43)	9(50)
O17	2547(8)	7533(11)	3492(9)	0.89	163(51)	55(54)	115(52)	-13(48)	-11(42)	-57(49)
O18	4120(9)	7286(12)	5515(9)	1.31	223(58)	178(61)	92(53)	31(50)	-4(45)	21(54)
O19	1792(9)	5953(13)	5893(11)	1.91	133(55)	272(68)	293(64)	-23(60)	-37(48)	81(58)
O20	3869(8)	-445(11)	2735(9)	0.94	145(55)	121(57)	97(53)	-52(46)	3(45)	-16(46)
O21	590(9)	4239(13)	1707(12)	2.28	264(64)	155(66)	408(74)	-240(60)	-130(57)	15(56)
O22	-221(8)	2983(12)	-290(10)	1.47	165(57)	184(61)	197(63)	76(49)	-39(47)	-61(49)
O23	-266(9)	1764(13)	1749(10)	1.59	173(58)	275(71)	136(58)	98(52)	-66(49)	-94(53)

Temperature factor = $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + hka^*b^*U_{12})]$

E.s.d. in parentheses.

TABLE 5. INTERATOMIC DISTANCES (standard deviations are near 0.01 Å)

Cu(1) octahedron		Cu(2) octahedron		Cu,Zn(3) octahedron		Cu,Zn(4) octahedron		Cu,Zn(5) octahedron	
Cu(1)-O(13)	2.94	Cu(2)-O(14)	2.73	Cu,Zn(3)-O(19)	2.49	Cu,Zn(4)-O(10)	2.43	Cu,Zn(5)-O(18)	2.50
O(10)	2.24	O(13)	2.15	O(10)	2.30	O(19)	2.37	O(16)	2.26
O(11)	2.03	O(15)	2.05	O(15)	2.01	O(20)	2.05	O(20)	2.05
O(12)	1.98	O(12)	2.03	O(17)	2.01	O(11)	2.01	O(11)	2.04
O(14)	1.97	O(16)	1.99	O(9)	1.99	O(17)	1.96	O(12)	2.00
O(9)	1.97	O(9)	1.99	O(18)	1.93	O(18)	1.95	O(17)	1.98
O(19)-O(11)	3.67	O(14)-O(15)	3.64	O(19)-O(9)	3.23	O(10)-O(20)	3.55	O(18)-O(12)	3.50
O(9)	3.41	O(12)	3.04	O(17)	3.17	O(18)	3.14	O(20)	2.95
O(12)	3.37	O(16)	2.96	O(18)	3.16	O(17)	2.95	O(17)	2.72
O(14)	3.22	O(9)	2.77	O(15)	2.96	O(11)	2.92	O(11)	2.66
O(10)-O(12)	3.34	O(19)-O(12)	3.37	O(10)-O(15)	3.39	O(19)-O(18)	3.16	O(16)-O(17)	3.37
O(14)	3.26	O(9)	3.31	O(18)	3.13	O(17)	3.14	O(11)	3.23
O(11)	2.92	O(16)	3.10	O(17)	2.95	O(20)	3.05	O(20)	2.99
O(9)	2.85	O(15)	2.96	O(9)	2.85	O(11)	3.03	O(12)	2.76
O(11)-O(9)	2.91	O(15)-O(12)	3.10	O(15)-O(18)	2.91	O(20)-O(18)	2.95	O(20)-O(12)	3.04
O(12)	2.58	O(9)	2.65	O(9)	2.65	O(17)	2.64	O(17)	2.64
O(14)-O(12)	2.93	O(16)-O(9)	3.02	O(17)-O(9)	2.94	O(11)-O(17)	3.01	O(11)-O(17)	3.09
O(9)	2.77	O(12)	2.76	O(18)	2.72	O(18)	2.66	O(12)	2.58
Zn(6) tetrahedron		P(7) tetrahedron		P(8) tetrahedron		H bonds ($d < 2.95 \text{ \AA}$)			
Zn(6)-O(16)	1.96	P(7)-O(13)	1.53	P(8)-O(10)	1.53	OH(9)-O(21)	2.77		
O(21)	1.91	O(21)	1.53	O(14)	1.54	OH(16)-O(13)	2.92		
O(22)	1.93	O(22)	1.55	O(15)	1.56	OH(17)-O(23)	2.85		
O(23)	1.93	O(23)	1.52	O(20)	1.55	OH(18)-O(14)	2.93		
O(16)-O(21)	3.50	O(13)-O(21)	2.49	O(10)-O(14)	2.53	H ₂ O(19)-O(13)	2.80		
O(22)	3.13	O(22)	2.55	O(15)	2.51	H ₂ O(19)-O(22)	2.69		
O(23)	3.17	O(23)	2.50	O(20)	2.51				
O(21)-O(22)	2.97	O(21)-O(22)	2.52	O(14)-O(15)	2.51	O(13)-O(19)-O(22)	129°		
O(23)	2.89	O(23)	2.50	O(20)	2.51	O(16)-O(13)-O(19)	119°		
O(23)	3.16	O(22)-O(23)	2.45	O(15)-O(20)	2.55				

TABLE 6. BOND VALENCES (v.u.) WITH THE SUMS Σ

	Cu(1)	Cu(2)	Cu*(3)	Cu*(4)	Cu*(5)	Zn(6)	P(7)	P(8)	H	Σ	
O(9)	0.44	0.43	0.43						-0.18	1.12	OH
O(10)	0.20		0.18	0.13			1.28			1.79	PO ₄
O(11)	0.37			0.40	0.37				-0.09	1.05	OH
O(12)	0.43	0.38			0.41					1.22	OH
O(13)	0.04	0.27					1.28		0.26	1.86	PO ₄
O(14)	0.44	0.06						1.25	0.10	1.85	PO ₄
O(15)		0.36	0.40					1.18		1.94	PO ₄
O(16)		0.43			0.20	0.50			-0.10	1.03	OH
O(17)			0.40	0.47	0.44				-0.13	1.18	OH
O(18)			0.51	0.48	0.11				-0.10	1.00	OH
O(19)			0.11	0.15					-0.38	-0.12	H ₂ O
O(20)				0.36	0.36			1.22		1.94	PO ₄
O(21)						0.58	1.28		0.27	2.13	PO ₄
O(22)						0.55	1.22		0.22	1.99	PO ₄
O(23)						0.55	1.32		0.13	2.00	PO ₄
Σ	1.92	1.93	2.03	1.99	1.89	2.18	5.10	4.93			

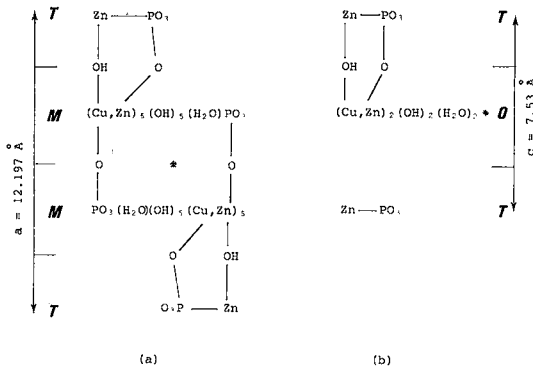
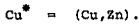


FIG. 4. Structural diagram for kipushite (a) and veszelyite (b) with tetrahedral (T), octahedral (O) and mixed (M) sheets. Centres of symmetry:*

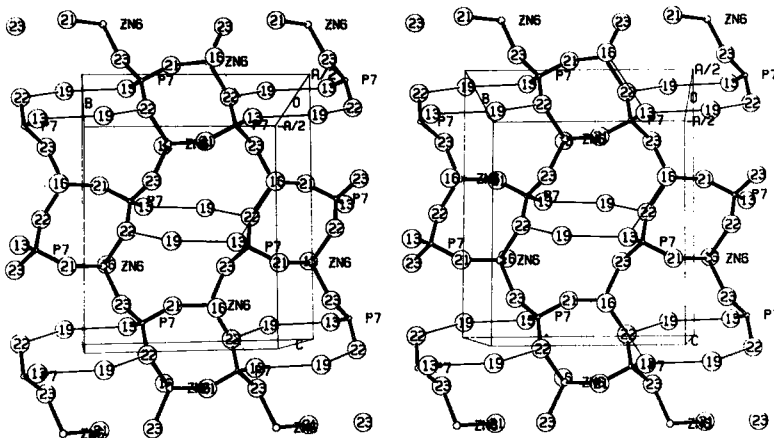


FIG. 5. Stereoscopic drawing (Johnson 1965) of the sheet of tetrahedra in kipushite. Thin lines indicate H bonds.

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The program SHELX 76 (Sheldrick 1976) was used for all calculations, with complex neutral-atom scattering-functions. Figures 5 and 6 were drawn with the program ORTEP (Johnson 1965).

DESCRIPTION OF THE STRUCTURE

The final atomic co-ordinates and temperature-parameters are given in Table 4. Interatomic distances are presented in Table 5. The estimated bond-valences (v.u.) are given in Table 6. They were calculated using the constants of Brown & Wu (1976). Account was taken of hydrogen bonds (Donnay & Allmann 1970). The sums of bond valences show clearly the distinction between O, OH and H₂O.

The structure consists of a sheet of tetrahedra $[\text{Zn}(\text{PO}_4)\text{OH}]_n^{2n-}$ with two mixed sheets $[(\text{Cu}, \text{Zn})_5(\text{OH})_5(\text{H}_2\text{O})\text{PO}_4]_n^{2n+}$ which include five octahedra around (Cu,Zn) and one tetrahedron around P. Structural diagrams for kipushite and veszelyite are given in Figure 4.

Sheet of tetrahedra

The sheet of tetrahedra (Fig. 5) is very similar to that in veszelyite (Ghose *et al.* 1974), and is built up of PO₄ and ZnO₃(OH) tetrahedra sharing corners. The P(7)O₄ tetrahedron is regular. The mean P-O distance is 1.53 Å (1.54 Å in veszelyite). The mean O-O distance is 2.50 Å (2.51 Å in veszelyite). This PO₄ tetrahedron shares 3 corners with ZnO₃(OH) tetrahedra, whereas the fourth corner [O(13)] is bonded to Cu(2) and, very weakly, to Cu(1).

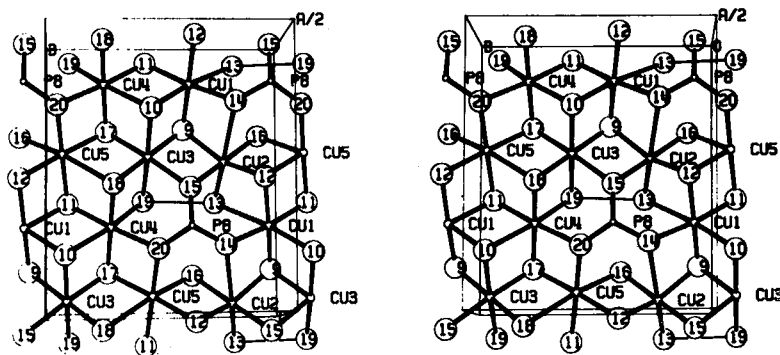


FIG. 6. Stereoscopic drawing (Johnson 1965) of the mixed octahedral-tetrahedral sheet in kipushite. Thin lines indicate H bonds.

The $\text{ZnO}_3(\text{OH})$ tetrahedron shows differences between distances from Zn to O or to OH. Means are: Zn-O 1.92 Å (1.94 Å in veszelyite), Zn-OH 1.96 Å (1.97 Å in veszelyite), O-O 3.01 Å (3.11 Å in veszelyite; for this mean, three erroneous distances given by the authors have been corrected), and (OH)-O 3.27 Å (3.20 Å in veszelyite). This tetrahedron shares three corners with PO_4 tetrahedra and the fourth [OH(16)] with Cu(2) and Cu(5).

Mixed octahedral - tetrahedral sheets

The mixed sheets (Fig. 6) are very compact. They do not have the empty cavities found in many other Cu or Zn phosphates and sulfates. This explains the relatively high density of kipushite, 3.90 g/cm³, compared to 3.42 g/cm³ in veszelyite, for instance.

The $\text{P}(8)\text{O}_4$ tetrahedron is regular. Mean distances are P-O 1.54 and O-O 2.52 Å. It shares three corners each with two Cu atoms of the same sheet. The fourth corner is bonded to three Cu atoms of the other mixed sheet.

The five octahedra possess a rather regular equatorial square (three OH and one O) around (Cu,Zn), with distances (Cu,Zn)-O between 1.93 and 2.05 Å [general mean: 2.00 Å, (Cu,Zn)-OH: 1.99, (Cu,Zn)-O: 2.03 Å], whereas the apical distances vary greatly. Co-ordination around Cu(1) may even be considered as a tetragonal pyramid, the sixth oxygen atom O(13) being located at the limit of the co-ordination sphere [Cu(1)-O(13) : 2.94 Å]. As this co-ordination is typical of Cu^{2+} (Jahn-Teller effect), it is unlikely that any Zn occupies this site. This situation is also found in veszelyite, with distances 2.47 and 2.93 Å around the first Cu, 2.45 and 2.47 Å around the second Cu. Distortion around Cu(2) is also important (2.15 and 2.73 Å); Cu rather than Zn probably occupies this site. The three other octahedra are more regular and, therefore, proba-

bly include the sites of the 1.14 Zn found by chemical analysis.

The salient features of the five octahedra are shown in Table 7. The two possible co-ordination numbers, 5 and 6, are considered for Cu(1).

Bonding between sheets

The two mixed sheets are linked by the common atom O(10) at the apex of a PO_4 group. Sheets of tetrahedra are linked to mixed sheets by O(13), at the apex of the other PO_4 tetrahedron, and by OH(16) at the apex of the $\text{ZnO}_3(\text{OH})$ tetrahedron.

In addition to these direct bonds, there are some hydrogen bonds (Table 5) between the mixed sheets: OH(18)-O(14), and between the mixed and tetrahedral sheets: OH(9)-O(21), OH(16)-O(13), OH(17)-O(23), $\text{H}_2\text{O}(19)$ -O(13) and $\text{H}_2\text{O}(19)$ -O(22).

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TABLE 7. DESCRIPTION OF THE FIVE (Cu,Zn) OCTAHEDRA

	1		2	3		4
	OH	PO	H ₂ O	Cu	Zn	P
Cu(1)	3	3	5	3	2	13
Cu(2)	3	2	4	1	3	12
Cu,Zn(3)	3	2	1	5	2	12
Cu,Zn(4)	3	2	1	5	2	12
Cu,Zn(5)	5	1	5	1	1	12

1. Nature and number of neighbors. 2. Number of shared edges. 3. Number of shared corners with Cu, Zn and P polyhedra. 4. Total number of external O-P, O-Zn and O-Cu bonds formed by the oxygen atoms of the polyhedron. For Cu(1), two co-ordination numbers (5 and 6) are considered (see text).

REFERENCES

- BERRY, L.G. (1948): Structural crystallography of lazulite, scorzalite and veszelyite. *Amer. Mineral.* **33**, 750 (abstr.).
- BROWN, I.D. & WU, KANG-KUN (1976): Empirical parameters for calculating cation-oxygen bond valences. *Acta Cryst.* **B32**, 1957-1959.
- BUTTGENBACH, H. (1927): Description d'un minéral du Katanga. *Bull. Acad. roy. Belgique, Cl. Sci.* **11-12**, 905-913.
- DONNAY, G. & ALLMANN, R. (1970): How to recognize O^{2-} , OH^- and H_2O in crystal structures determined by X-rays. *Amer. Mineral.* **55**, 1003-1015.
- GHOSE, S., LEO, S.R. & WAN, C. (1974): Structural chemistry of copper and zinc minerals. 1. Veszelyite $(Cu,Zn)_2ZnPO_4(OH)_3 \cdot 2H_2O$: a novel type of sheet structure and crystal chemistry of copper-zinc substitution. *Amer. Mineral.* **59**, 573-581.
- INTIOMALE, M.M. & OOSTERBOSH, R. (1974): Géologie et géochimie du gisement de Kipushi, Zaïre. In *Gisements Stratiformes et Provinces Cuprifères. Volume du Centenaire*, Soc. géol. Belgique, Liège, 123-164.
- JOHNSON, C.R. (1965): ORTEP. *Oak Ridge Nat. Lab., Rep.* **ORNL-3794**.
- LARSEN, E.S. (1921): The microscopic determination of the nonopaque minerals. *U.S. Geol. Surv. Bull.* **679**.
- MANDARINO, J.A. (1981): The Gladstone-Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.
- MENNELL, F.P. & SPENCER, L.J. (1920): Rare zinc-copper minerals from the Rhodesian Broken Hill mine, northern Rhodesia. *Mineral. Mag.* **19**, 69-72.
- OHASHI, R. (1924): On daiton-sulphur, arakawaite and ishikawaite. *J. Geol. Soc. Tokyo* **31**, 166-170.
- PALACHE, C., BERMAN, H. & FRONDEL, C. (1951): *Dana's System of Mineralogy*. II (7th ed.). J. Wiley & Sons, New York.
- SCHRAUF, A. (1880): Über Phosphorkupfererze. *Z. Krist. Mineral.* **4**, 1-33.
- SHELDRIK, G.M. (1976): *Program for Crystal Structure Determination*. University of Cambridge, England.
- WAKABAYASHI, Y. & KOMADA, K. (1921): A phosphate of copper and zinc from Arakawa mine. *J. Geol. Soc. Tokyo* **28**, 191-211.
- ZSIVNY, V. (1930): Über den Veszelyit von Vaskö (Moravicza) und seine Stellung zum Arakawait und Kipushit. *Int. Geol. Congress 15th (South Africa)* **2**, 438.
- _____ (1932): Über den Veszelyit von Vaskö (Moravicza). *Mat. Termès. Ertesitö, Budapest* **48**, 331-358.

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